EXAM 1

23 September 2002

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.

Give units for all quantities!

Some data: $R = 8.314\ J\ K^{-1}\ mol^{-1}$ 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23}\ mol^{-1}$

YOUR NAME SOLUTIONS

(1) *30 points*

(a) The compression factor for ethylene is about 1.3 at p = 300 bar, about 0.6 at p = 100 bar, and tends to 1 exactly as p tends to zero. Give a brief, qualitative explanation. Feel free to draw any picture(s) that might help.

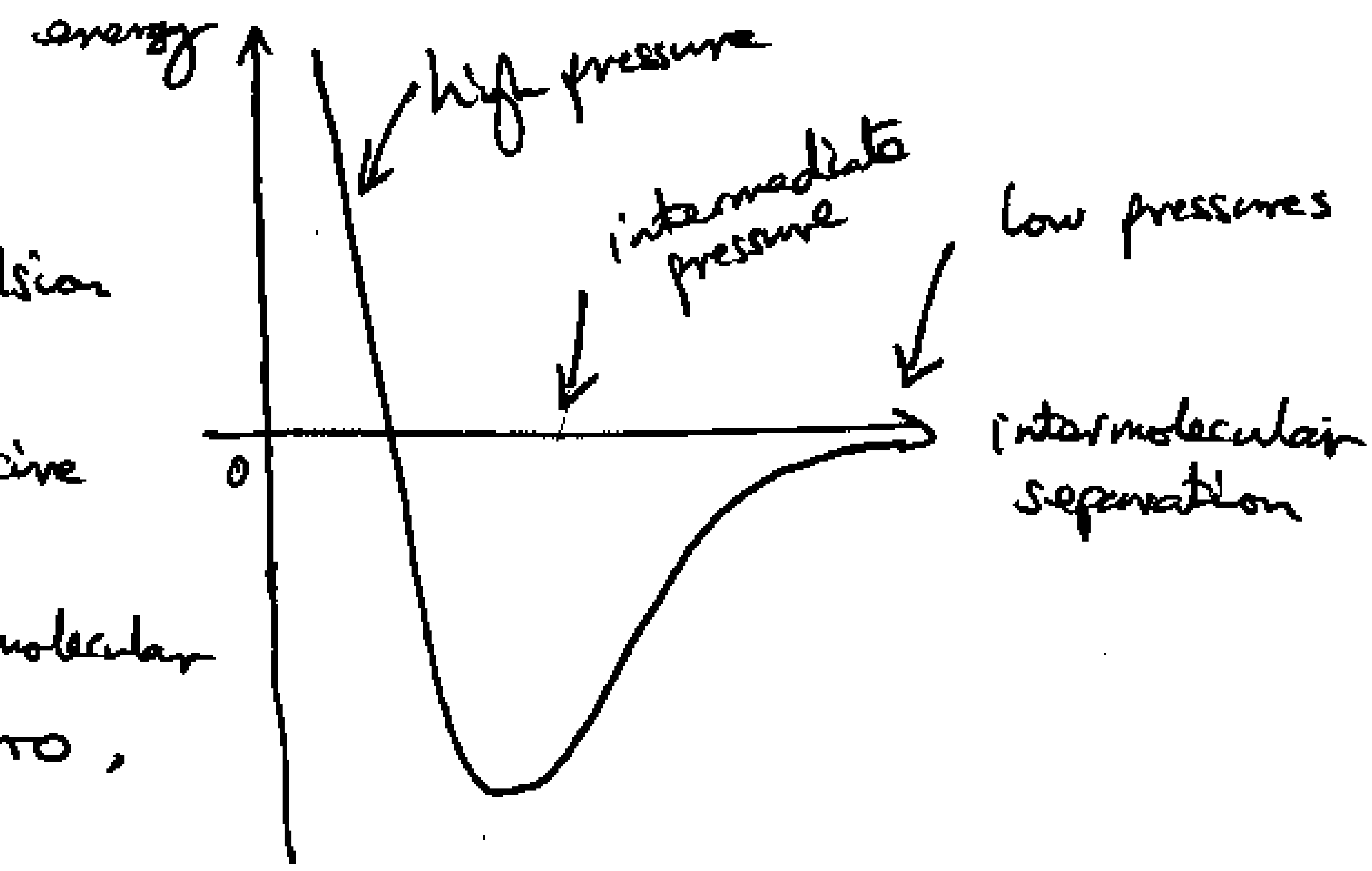
(b) A real gas (the system) with the following equation of state

$$p = nRT/(V-nb) - a(n/V)^3$$

is expanded reversibly and isothermally from V_1 to V_2 at temperature T. Calculate the work w done on the system.

a) See notes.

At very high pressures repulsion dominates and $Z>1$.
At moderate pressures attractive forces dominate and $Z<1$.
At very low pressures intermolecular forces become close to zero.



b) $dw = -p_{ex}dV = -pdV$ here (reversible).

$$\therefore w = -\int_{V_1}^{V_2} p\,dV = -\int_{V_1}^{V_2} \frac{nRT}{V-nb}\,dV + \int_{V_1}^{V_2} a\left(\frac{n}{V}\right)^3 dV$$

$$= -nRT\left[\ln(V-nb)\right]_{V_1}^{V_2} - \frac{an^3}{2}\left[\frac{1}{V^2}\right]_{V_1}^{V_2}$$

$$= nRT\ln\left(\frac{V_1-nb}{V_2-nb}\right) + \frac{an^3}{2}\left(\frac{1}{V_1^2} - \frac{1}{V_2^2}\right)$$

(2) *30 points*

Elemental sulfur, $S(s)$, reacts with elemental fluorine, $F_2(g)$, in a constant volume calorimeter to make $SF_6(g)$. C_p for these three substances is 20, 30-1000/T and 100-8000/T. The heat released from calorimeter is 600 kJ per mol of S consumed at 298 K. Calculate

(a) $\Delta_f H_{298}$ of $SF_6(g)$.

(b) $\Delta_f H_{1100}$ of $SF_6(g)$.

(c) ΔH_{298} for the reaction $S_3F_4(g) + 7\,F_2(g) \rightarrow 3\,SF_6(g)$, given that $\Delta_f H_{298}$ of $S_3F_4(g)$ is -150 kJ mol^{-1}.

a) For $S_{(s)} + 3F_{2(g)} \longrightarrow SF_{6(g)}$ $\quad \Delta U = -600\ \text{kJ mol}^{-1}$.

$$H = U + pV \therefore \Delta H = \Delta U + \Delta(pV) \approx \Delta U + RT\,\Delta n_{gas}$$

$$= \Delta U - 2RT$$

$$= -600 - \frac{2 \times 8.314 \times 298}{1000}\ \text{kJ mol}^{-1}$$

$$= -605\ \text{kJ mol}^{-1}.$$

This is $\Delta_f H_{298}\,(SF_{6(g)})$

b) $$\Delta H_{1100} = \Delta H_{298} + \int_{298}^{1100} \Delta C_p \,dT.$$

$$\Delta C_p = 100 - \frac{8000}{T} - 20 - 3\left(30 - \frac{1000}{T}\right) = -10 - \frac{5000}{T}.$$

$$\int_{298}^{1100} \Delta C_p\,dT = \Big[-10\,T - 5000 \ln T\Big]_{298}^{1100}$$

$$= -11000 + 2980 - 35015 + 28485\ \text{J mol}^{-1}$$

$$= -14550\ \text{J mol}^{-1}$$

$$\therefore \Delta_f H_{1100} = -605 - 14.6\ \text{kJ mol}^{-1} \approx -620\ \text{kJ mol}^{-1}.$$

c) $S_3F_{4(g)} + 7F_{2(g)} \longrightarrow 3SF_{6(g)}$

$\Delta_f H_{298}$	-150	0	-605×3	kJ mol^{-1}

$$\Delta H_{298} = -1815 + 150\ \text{kJ mol}^{-1} = -1665\ \text{kJ mol}^{-1}.$$

(3) *40 points*

1 mol of an ideal gas with $C_p = 25\ J\ K^{-1}$ is initially at 298 K. It is confined in a cylinder of cross-sectional area $1 \times 10^{-3}\ m^2$ at a pressure of 10^6 Pa. A piston moves out 0.3 m and the gas expands adiabatically. Calculate w, q, ΔU, ΔH for the gas, and its final temperature, when

(a) The experiment is carried out irreversibly against a constant external pressure of 10^5 Pa.

(b) The expansion is carried out reversibly.

a) $q = 0 \therefore \Delta U = w = -P_{ex}\Delta V = -10^5\ Pa \times 1\times10^{-3}\ m^2 \times 0.3\ m$

$= -30\ J$.

$C_V = C_p - R = 16.69\ J K^{-1}$.

$\Delta U = C_V \Delta T \therefore \Delta T = -1.80\ K$,

$T_{final} = 298 - 1.8 = 296.2\ K$.

$\Delta H = C_p \cdot \Delta T = -45\ J$.

b) $P_1 V_1 = nRT_1 \therefore V_1 = \frac{nRT_1}{P_1} = \frac{8.314 \times 298}{10^6}\ m^3 = 0.002478\ m^3$.

$V_2 = V_1 + 10^{-3}\ m^2 \times 0.3\ m = 0.002778\ m^3$.

$\gamma = C_p / C_V = \frac{25}{25 - 8.314} = 1.498$.

$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \therefore P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{\gamma} = 10^6\ Pa \times 0.8427 = 8.427 \times 10^5\ Pa$.

$T_2 = \frac{P_2 V_2}{nR} = 281.6\ K$.

$\Delta T = -298 + 281.6\ K = -16.4\ K$.

$\Delta U = C_V \Delta T = -274\ J = w$ because $q = 0$.

$\Delta H = C_p \cdot \Delta T = -410\ J$.